

Fourier Spectroscopy of Planets

Michelson interferometers have recently begun to produce remarkably fine infrared spectra of planets.

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During the last year or two spectroscopists interested in the planets have been amazed by some new near-infrared spectra of a resolution and quality previously available only for the shorter wavelengths. In fact, the Venus spectra are better than the solar spectrum in the well-known "Michigan Atlas" (1) of the near-infrared region. (We must admit, however, that this atlas is some 20 years old; similar equipment could now produce considerably better spectra.) The detail in quite recent grating spectra of the region between 1 and 3 microns could readily be represented on a single page of this journal and were at the limit of the art. The new spectra, plotted on a 30-centimeter recorder chart, stretch all around the walls of a seminar room, and even this format barely does justice to the information. The word "breakthrough" is becoming rather stale these days, but it properly applies with full force to the development which we describe here.

The instrument that recorded the spectra is a Michelson interference spectrometer or Fourier spectrometer. Since the instrumentation is not new, the question may well be asked, "Where is the breakthrough?" Although the theoretical possibility has been known for over 20 years and can be traced back to Michelson himself, the credit belongs almost entirely to a French team of husband and wife, Pierre and Janine Connes. They have patiently tracked down each of the perturbations

that had caused departures from simple theory. With the elimination of the last perturbation, the spectra were promptly obtained. We shall describe this simple theory and then discuss the various perturbations and remedies developed by Pierre Connes, the experimentalist of the team.

Figure 1 shows the familiar Michelson interferometer. To it have been added source and exit optics, as in any spectrometer, and beyond the exit diaphragm is a photoelectric detector. The beam splitter divides the incident radiation into two, nominally identical, beams; the compensating plate, inserted in the beam which does not traverse the material of the beam splitter, maintains the similarity of the two paths. After reflection from the mirrors, the two beams are recombined at the beam splitter, and the resultant beam is detected. If the two paths are of identical length, constructive interference occurs for all wavelengths.

Fourier-Transform Spectroscopy

One mirror is translated at a slow, uniform rate, while remaining accurately parallel to the image of the fixed mirror. Each wavelength of the radiation will undergo first destructive, and then constructive, interference; one complete cycle is traversed for a mirror displacement of half a wavelength. The output of the detector, recorded as a function of displacement, is called an interferogram. The inter-

ferogram is the Fourier transform of the spectrum of the detected radiation. The origin of the term Fourier spectroscopy is clear. A computer routine for Fourier transformation can convert the interferogram into a spectrum.

The process is readily understood if one considers one, or just a few, discrete wavelengths. The interferogram of a monochromatic source is a simple, pure cosine function. The period, in terms of mirror displacement, is equal to half the wavelength. The interferogram of a real source is the sum of all the elementary cosines for the various wavelengths present. The process of Fourier transformation (or inversion) may be thought of as a frequency analysis that obtains the amplitude of each cosine wave.

Another useful viewpoint is to regard the Fourier spectrometer as a frequency transformer. Each very large optical frequency present in the incoming signal is shifted to a corresponding lower frequency, typically in the audio range or lower. These frequencies can then be analyzed by standard electronic and numerical techniques.

Suppose the spectrum consists of two closely spaced lines of equal intensity. The interferogram will then show beats as the two cosines go in and out of phase; from the period of the beats the spacing between the lines can be derived. This experiment has been popular in undergraduate optics laboratories, with the D lines of sodium as source and the student's eye as detector. The term interference fringes, common in such visual work, is often carried over when photoelectric detection is used. Or suppose the spectrum contains a single line with a finite width. Now, as the path difference increases, the amplitude of the fringes slowly decreases, and eventually the fringes disappear. The wider the line is, the earlier the disappearance; fairly good inferences about the line width can be obtained without any Fourier transform, although the same concepts are still applicable. The required optical path difference (twice the carriage motion), expressed in units of the wavelength, is just the ratio of the wavelength to the width of the line.

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These methods were used by Michelson to establish the purity of the red line of cadmium, which served as a standard of length until the recent introduction of lamps which contain artificial or separated isotopes. Another achievement was the inference of the hyperfine structure of atomic hydrogen. But as diffraction gratings and Fabry-Perot spectrometers achieved the ability to produce high-resolution spectra directly, the Fourier method came to be considered an interesting curiosity.

The revival of Fourier spectroscopy resulted from the increasing popularity of electrical detection, which is indeed the only possibility in most of the infrared region. Spectroscopists had been used to photographing a whole spectrum at once on a single plate. They resented the need to scan, one wavelength at a time, while being unable to use the rest of the radiation. Thinking over these difficulties, Fellgett (2) realized that the photoelectric Michelson interferometer detects all wavelengths simultaneously and thus is a multiplex device. A spectral region that extends from λ_1 to λ_2 , which is to be measured with resolution $\Delta\lambda$, contains $M = (\lambda_2 - \lambda_1) / \Delta\lambda$ spectral elements. If all spectral elements are detected simultaneously instead of in sequence, a measurement of a given quality can in principle be made in a time shorter by the factor $1/M$. If M is large, the advantage is enormous; it has come to be called the Fellgett advantage. Clearly, the gain is most important with high-resolution spectra.

Mechanical and Optical Refinements

The intervening 20 years have seen the gradual elimination of the factors that prevented the immediate realization of the Fellgett advantage. As always when a simple theory fails, the problem is that simple equipment requires complicated theory. It takes complicated equipment to operate according to simple theory, even if the complications may not be obvious to casual users. We shall now discuss some of the principal problems and qualifications.

The most obvious requirement is optical and mechanical quality and smoothness. The tolerance on the flatness of the mirrors is rather relaxed; they require a flatness that is little better than a quarter of the shortest wavelength. But they must maintain their angular alignment to rather better accuracy, even while one of them is being translated over a considerable dis-

tance. Such tolerances are readily maintained in the far-infrared region, where the wavelength approaches a tenth of a millimeter. Here we are mainly concerned with wavelengths as short as a micron, and it is usual to replace the plane mirrors by precision retroreflectors. These devices reverse an incoming beam by exactly 180° , and this reversal is independent of small rotations of the reflector. Conceptually, the simplest retroreflector is a cube-corner, composed of three plane mirrors mutually at right angles. In practice, a cube-corner is extremely difficult to make, because the three surfaces must be perpendicular to approximately one second of arc. For infrared work which requires front-surface mirrors wherever possible, three separate pieces of glass must be mounted to the required tolerance, with the smallest possible cracks where they join. Thus, although cube-corner interferometers have been made, they are rare.

A more practical device, first used in an interferometer by Connes, is a "cat's eye," named after a common, naturally occurring retroreflector (which works on still another principle). As Fig. 2 illustrates, a cat's eye resembles a Cassegrain telescope, but the surface of the secondary mirror passes through the focus of the primary. Normally, the primary is a paraboloid; the secondary may be planar, but there are advantages in making it convex and concentric with the primary (3). The spacing of the mirrors is critical, and their relative orientation must be closely maintained. Nevertheless, the cat's eye is more practical than a cube-corner and much less sensitive to small rotations than a plane mirror. The cat's eye also was used by Michelson, although not in interferometers and not under that name. When he measured the speed of light over a 35-kilometer path from Mount Wilson, the retroreflector on the other peak was a large cat's eye (4).

Even with retroreflectors, it is still necessary to drive the moving mirror with sufficient accuracy and smoothness. Again, in the far-infrared region the required performance is easily achieved with a sliding carriage driven by a lead screw. But at short wavelengths the best results have been obtained by referring the carriage position to the interference fringes from a laboratory line source, such as a mercury-198 lamp or a laser. The resulting performance is remarkable: not only are the spectra essentially free of perturbations, but the absolute accuracy of all

the wavelengths is limited only by the line widths, since they are all measured in terms of an accurately known standard wavelength. The spectrometer contains the near equivalent of a grating engine under interferometric control.

The actual practice is to pass the light of the standard line through the optical system of the interferometer itself. In general, the area of the optical system has been much greater than the area of the light beam from a telescope; it has therefore been possible to separate the reference beams from the measurement beams. This separation is facilitated by a property of retroreflecting mirrors: a beam that enters to one side of the axis (but parallel to it) emerges on the opposite side (5).

Source Fluctuations

Once the requirements of optical and mechanical precision have been met, a much more subtle difficulty remains. The fundamental virtue of the Fourier spectrometer is its multiplex property, which permits the simultaneous measurement of many wavelengths. Thus, the number M of spectral elements is normally very large; a typical value might be 10^4 in high-resolution work. The detector must be able to measure each element in the presence of the disturbances contributed by all the other elements. Unfortunately, in astronomical work there are disturbances that occur simultaneously at all wavelengths; in the worst cases these are caused by clouds, but they may also be scintillations caused by optical inhomogeneities in a perfectly clear atmosphere. If M is 10^4 , a modulation of only 0.1 percent will cause a perturbation ten times greater than the amplitude of a single spectral element. For 1 percent accuracy in each element, the incoming flux must remain constant to one part in 10^6 , or variations must be compensated to this final accuracy. The difficulty is a fundamental one, inherent in the basic virtue of the multiplex method: the more spectral elements there are, the worse are the problems.

The effect is illustrated more quantitatively by Fig. 3, which shows the general appearance of an interferogram from a continuous source. The large oscillations near a path difference of zero correspond to the white-light fringes of visual observation. The curve soon settles down to minor, apparently random, oscillations about a mean which is half the height of the central

peak. (This value differs from one half in usual practice, because the beam splitter seldom produces two equal beams.) Any modulation of the source will appear in the mean, and the change can readily be much greater than the tiny ripples that convey the spectral information.

A simple remedy is to scan the interferogram at a sufficiently high rate. If the source fluctuations occur in a time longer than the length of a scan, they have little effect on the results. A large number of successive scans may be added to obtain the required observing time for a good signal. This scheme has been pioneered by Mertz (6) and is incorporated into a number of small instruments. Unfortunately, the scan times required are well under a second, and such fast scans are incompatible with a really precise and reproducible motion. The best resolving power that has been demonstrated by a rapid-scanning interferometer is a few hundred, and the number of spectral elements is similar. Kuiper (7) has used an interferometer

designed by Mertz in a high-altitude aircraft to obtain excellent medium-resolution spectra of Mars and Venus, nearly free of terrestrial absorption of water vapor.

Connes has taken a number of steps to compensate for the fluctuations of the source. The first, suggested long ago by Fellgett, is to use two exit beams and take the difference between the outputs of the two detectors. The large mean of Fig. 3 is reduced to a value near zero. In the classical Michelson interferometer of Fig. 1, the second beam returns to the source and cannot be used. But in a cat's-eye interferometer the entrance and exit beams can be laterally displaced, and both exit beams can be used (Fig. 2). In practice the compensation is imperfect, because the detectors cannot be identical and frequently are not uniform over their sensitive areas. A second step is to split off some of the incoming light to still another detector that monitors the total flux; the output of the interferometer is then divided by the output of the

monitor. In the Connes scheme the interferometer carriage stops at each point, and the two signals are integrated. When the monitor output reaches a preset value, the other output is recorded.

Although these procedures lead to a considerable improvement, some perturbations are still present. According to Connes, the remaining difficulties are traceable to nonuniformities of the detectors, coupled with the uncorrelated fluctuations of the light in different parts of the planetary image. His first remedy was a beam scrambler, a tube with highly reflecting inside walls, through which the light was passed in the manner of a light pipe. But really complete scrambling of a beam is very difficult, especially if there is no light to be wasted. It was still necessary to limit the number of spectral elements in each run by means of a filter. A few planetary spectra were obtained with this equipment in 1965. Although they were much better than any previously available, these spectra still fell far short of the most recent results.

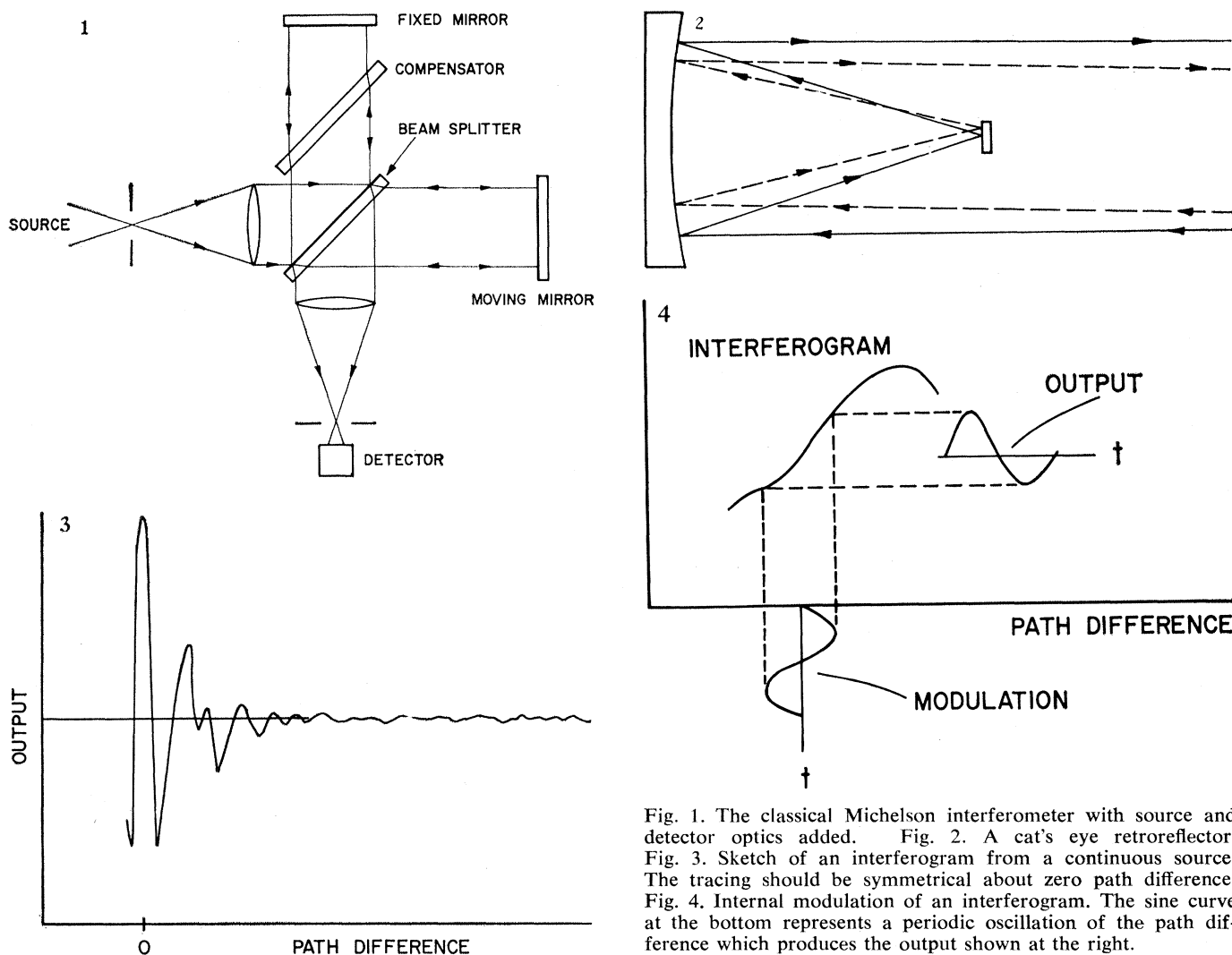


Fig. 1. The classical Michelson interferometer with source and detector optics added. Fig. 2. A cat's eye retroreflector. Fig. 3. Sketch of an interferogram from a continuous source. The tracing should be symmetrical about zero path difference. Fig. 4. Internal modulation of an interferogram. The sine curve at the bottom represents a periodic oscillation of the path difference which produces the output shown at the right.

Internal Modulation

In the paper that described this situation, the Connes team also pointed to the final solution of the problem (5). The original idea was suggested by Mertz, but its full reduction to practice was delayed for many years. The technique has been named internal modulation, a term that requires some explanation. Figure 4 shows a small section of an interferogram; the sine wave at the bottom corresponds to a small, rapid modulation of the path difference. If the amplitude is small, the detector will produce, at the modulation frequency, an output proportional to the derivative of the interferogram. In practice, the peak-to-peak amplitude of the modulation is fairly large, about half a typical wavelength; the corresponding distortion is readily allowed for. Similar modulation schemes are used in many fields of investigation, for example, nuclear magnetic resonance and microwave spectroscopy. The derivative of the interferogram may be obtained by the standard technique of synchronous demodulation (or phase-sensitive detection). The phase reversal which corresponds to a negative slope changes the sign of the output from such detectors.

The important result is that the mean value of the derivative is zero, so that disturbances of the mean level have little effect on the individual Fourier components. The difficulty with the

large mean of the normal interferogram is removed, as long as the modulation frequency is high enough; several cycles must elapse during the time typical of the perturbations. Since this time is several tenths of a second (for astronomical scintillation), a frequency of a few hundred cycles per second is suitable; Connes and co-workers use 200 cycles (5).

As Mertz has pointed out (6), the amplitude of the internal modulation must be stable, for any variations will be reflected into the interferogram. Nevertheless, the effect is tolerable, because it is not multiplied by the number of spectral elements. With an amplitude close to the optimum value, the variations are greatly suppressed. In practice, the difficulty is not particularly severe. Much more troublesome is the tendency for the mechanical vibrations of the modulator to be coupled directly into the detectors or to other parts of the optical system. Connes and co-workers went as far as to use separate mounting bases for the interferometer and the modulator.

The modulator that has been used consists of a pair of thin, inclined plates mounted on the ends of a tuning fork. As the fork vibrates, the angles of the plates change slightly, and the path length through them changes accordingly. The assembly is inserted in one of the paths, and a similar, but fixed, pair is inserted in another path. An important advantage of this technique

is that the reference beams are not modulated and their fringes are unaffected. Perhaps a more elegant scheme would be to vibrate the small secondary mirror of one of the cat's eyes; a piezoelectric ceramic element would be suitable. But the reference system would be modulated as well, and at a large amplitude, because the wavelength used is normally much shorter than those being measured. It will no doubt be possible to find a way around this difficulty, but considerable work may be required.

An interesting limitation of multiplex methods is that the Fellgett advantage does not apply when the detector is a good photomultiplier. Such tubes (refrigerated if necessary) have a negligible dark current. The only significant source of noise is the shot noise caused by the limited numbers of photoelectrons that correspond to a spectral element. If this number is N , the root-mean-square fluctuation is $N^{1/2}$, and the signal-to-noise ratio has the same value. Let us suppose that the N electrons are obtained in conventional, simplex spectrometry and that a time t is required to scan a spectral element; the total spectrum will require a time Mt . In the corresponding multiplex instrument a similar measurement is made of all M spectral elements for the same total time. The number of photoelectrons accumulated for each element is now NM . But the noise must be calculated from the total signal, which is NM^2 ; the root-mean-square fluctuation is therefore $MN^{1/2}$. The ratio of signal to noise is $N^{1/2}$, exactly the same as for the simplex spectrometer; the noise has increased by the same factor as the signal. The multiplex advantage applies only when the detector noise is independent of the signal, as for nearly all infrared detectors. In special cases the other advantages of the Fourier method might still dictate its use with photomultipliers; for example, refrigeration could be dispensed with, and advantage could be taken of the good instrumental function and accurate wavelength scale.

Fourier spectroscopy is still not the remedy for the inefficiency associated with scanning a spectrum at visible wavelengths. Television tubes, such as the image orthicon, have in principle the required properties. Although the high sensitivity has been used for auroral photography and spectroscopy, the measurements are so far only semi-quantitative, and the technique has found little application in astronomy (8).

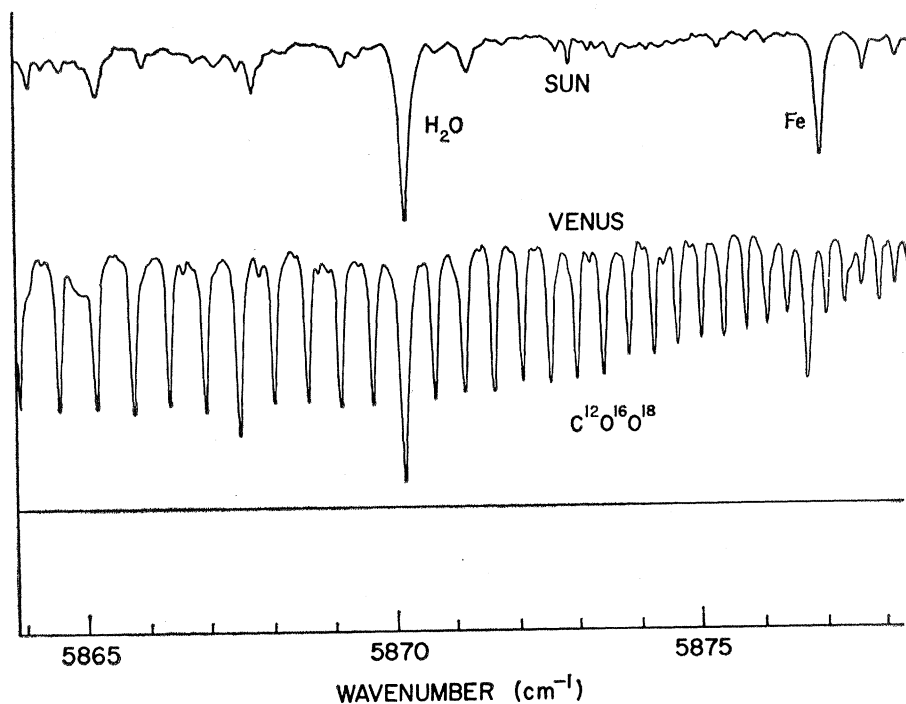


Fig. 5. A very small part of one of the Connes spectra of Venus, along with a solar spectrum displaced upwards.

Examples

Figure 5 shows a very small section of one of the Connes spectra of Venus, along with a solar comparison. The solar, as well as planetary, lines show a Doppler displacement from the relative motion of Earth and Venus; terrestrial lines remain at the same position. The planetary lines seen here belong to a band of CO_2 (in which one oxygen atom is the rare isotope, O^{18}). The best grating spectra of Venus, with slit widths comparable to the whole width of Fig. 5, show this band only as a weak, smooth depression which does not provide a positive identification.

The wealth of detail in these spectra has been under study (9). The most remarkable result has been the discovery of traces of HCl and HF. The HCl band shows both chlorine isotopes in the usual ratio. These discoveries provide an excellent illustration of the power of high-resolution infrared spectroscopy. Not only can very small amounts be detected (the proportion of HF is 5×10^{-9}), but also there is no question of the proper identification. The implications for planetary physics are only beginning to be explored. For example, Lewis has pointed out that any liquid water in the clouds must actually consist of rather strong hydrochloric acid (10).

Carbon monoxide, previously suspected on the basis of a marginal absorption band found by Sinton, shows its presence by many bands of assorted isotopic composition. Carbon dioxide bands were discovered long ago by Adams and Dunham in the near-infrared region and have been the subject of intensive study in the last few years (11). The Connes spectra show 190 CO_2 bands, including seven different isotopic species; the isotopic ratios in carbon and oxygen are the same as on Earth.

Equally fine spectra for Mars are in existence, but little has yet been said of any results. The presence of small amounts of CO is clear. Stellar spectra have also been obtained; molecular bands are present here also and show a remarkable development of rotational and vibrational levels at the high temperature.

More recently, Hanel has observed Venus in the region from 8 to 13 microns, where the radiation originates as thermal emission from the planet (12). The similar emission from Earth's atmosphere was allowed for by sub-

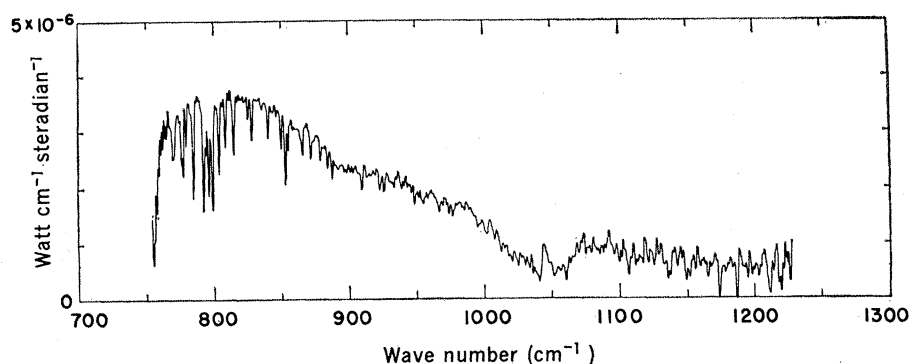


Fig. 6. A spectrum of Venus in the 10-micron region. [Courtesy of R. Hanel and the *Journal of Atmospheric Sciences*]

traction. The resulting spectrum is shown in Fig. 6; the major feature (at 1050 cm^{-1}) is an O_3 band caused by absorption in the Earth's atmosphere. The ratio of Venus and lunar spectra appears in Fig. 7; here the O_3 band reveals itself as a large increase in the noise level. Clearly, there is little structure in this region of the Venus spectrum, apart from the CO_2 band at 791 cm^{-1} and a broad dip at about 890 cm^{-1} . Such information bears on models of the temperature profile in the part of the atmosphere and clouds that emits the thermal radiation; the problem becomes analogous to that of a stellar atmosphere in the visible region.

Conclusion

It should be emphasized that observations such as these consume a great amount of viewing time on large telescopes, and that competition for this time is very great. Both Connes and Hanel have been able to obtain adequate time only because of unusual circumstances that will not often recur. But a high-quality, general-purpose telescope is not really needed; the interferometer can accept a fuzzy beam just as well as a sharp one. Special-purpose

"light-buckets," of inexpensive construction, are satisfactory, and several projects of this kind are now being considered; Connes, in particular, is well advanced in such a project.

The new developments have made it possible to obtain high-resolution spectra from bright objects. The limitation is now the inherent signal-to-noise ratio; higher resolution will require more light obtained by bigger mirrors or longer observing time. For fainter objects the attainable resolution rapidly decreases, and much simpler Fourier spectrometers are still adequate. Examples are the instrument of Sinton, based on birefringent crystals (11), and the compact interferometer of Mertz (6).

The problem of the Fourier transformation deserves at least a brief mention. Michelson constructed a mechanical "harmonic synthesizer" for the purpose, and this lead is still being followed by a number of investigators, who are using electronic, instead of mechanical, analog computers built for the purpose (13). But as these devices improve, the power and speed of general-purpose digital computers has kept pace, and most transformations are being made by computers. The trend has been greatly accelerated by the development of fast Fourier transform

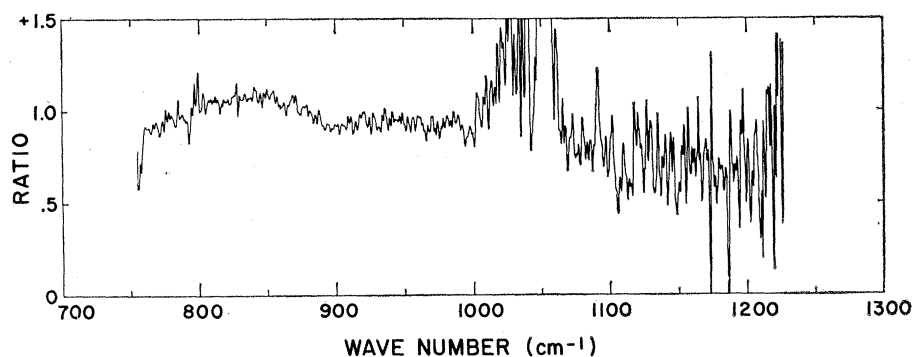


Fig. 7. Ratio of the Venus spectrum of Fig. 6 to a lunar spectrum. [Courtesy of R. Hanel and the *Journal of Atmospheric Sciences*]

techniques, such as the Cooley-Tukey algorithm. Although we do not discuss the details here, the subject of Fourier spectroscopy is as full of pitfalls on the mathematical side as on the experimental (14).

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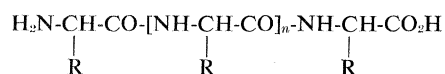
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Chemical Cleavage of Proteins

Selective fragmentations and modifications reveal structure.

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Proteins, such as enzymes, hormones, immunoglobulins, or the structural tissue component collagen, are biopolymers composed of about 20 different amino acids. The repeating sequence



is held together by the amide group as the covalent link. The aim of the protein chemist is to establish the primary structure, that is, the correct order of all amino acids in the chains between the amino-terminal and the carboxy-terminal residues. Proteins are digested, that is, hydrolyzed, by specific mammalian enzymes (trypsin, chymotrypsin), by less specific plant and animal enzymes (papain, pepsin, elastase), or by very aggressive bacterial enzymes (pronase, subtilisin) which hydrolyze all peptide bonds indiscriminately. The chemical cleavage of the amide or peptide group requires strong acid or base and elevated temperature.

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By controlling the conditions of acid hydrolysis, Emil Fischer was able to show that, for instance, silk fibroin which is rich in serine, easily breaks down into peptides—aggregates of two, three, or more amino acids which reveal part of the sequence of the original protein (1). The extension of this principle, the matching of a sufficient number of overlapping peptides, permits the establishment of the complete primary sequence of a protein. Historically, the sequences of the A and B chains of the protein hormone insulin with a total of 51 amino acids were first elucidated in this fashion (2).

Selective nonenzymatic cleavage: cyanogen bromide reaction. A much larger protein is the hormone that regulates and controls growth in humans (Fig. 1) (3). It contains 188 amino acid residues. In such a protein, tryptic digestion alone, that is, hydrolysis by trypsin, which breaks the protein at the arginine and lysine residues, would lead to a complicated mixture of peptides and to a major problem of separation. Cyanogen bromide (Br-C≡N), a simple chemical reagent, permits almost

quantitative cleavage (4, 5) next to the three methionine residues, Met(14), (122), and (167). The four peptide fragments formed in this reaction are separable by column chromatography and are then amenable to individual sequence analysis by enzymatic digestion (3). No generally usable enzymatic cleavage is known which would be of comparable selectivity. Such a reagent makes possible and simplifies the arduous task of "sequencing" large proteins with molecular weights as high as 50,000 to 150,000, that is, with about 500 to 1500 individual amino acids (Table 1) (6).

Besides aiding in the establishment of the primary sequence, the products of cyanogen bromide cleavage provide answers to other questions, such as whether the activity of human growth hormone resides in the entire structure or whether it is possible to have smaller active fragments (7). Adrenocorticotrophic hormone (ACTH), which contains 39 amino acids, requires only 23 amino acids for physiological activity (8) as established by synthesis.

Rabbit immunoglobulin of type G (IgG) with a molecular weight of 150,000, is cleaved by cyanogen bromide (9), as well as by papain and pepsin. From an immunological point of view, this reduction in size has advantages. All its undesirable properties, such as complement fixation, skin binding, and reaction with antiglobulin factors, stay in the fragments which remain on the column on gel filtration (10). The eluted smaller immunoglobulin may now be an improved natural therapeutic agent whose practical application is open to clinical testing. Cleavage by cyanogen bromide of 18 of the 20 methionyl peptide bonds in the two heavy (mo-